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(54) Title: LOW MELTING POLYALKYLENEPOLYAMINE CORROSION INHIBITORS

$$H_2N-CHR^1-CHR^2-N-CHR^3-CHR^4-NH_2$$
$$|$$
$$H$$
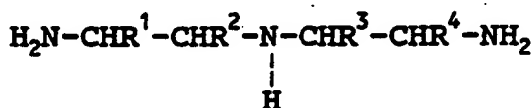
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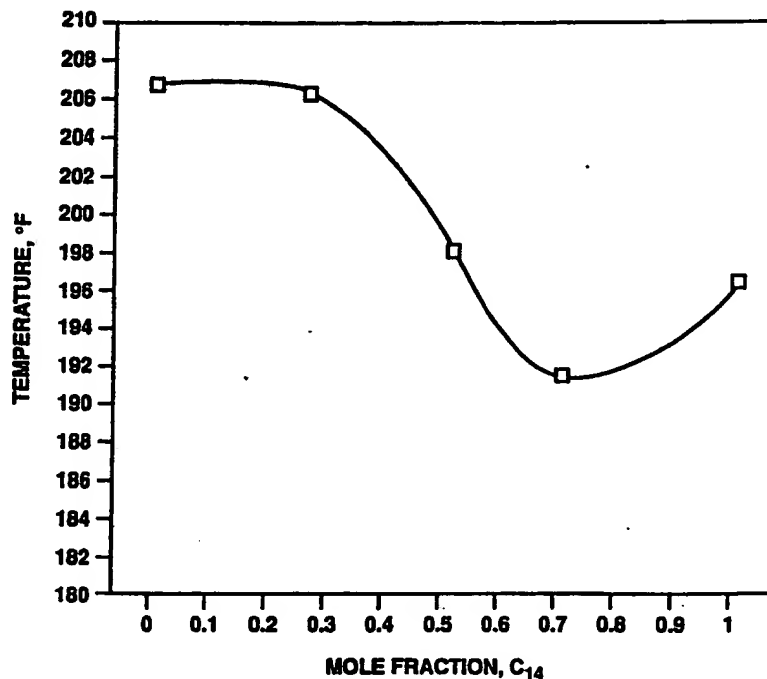
(57) Abstract

Disclosed are polyalkylenepolyamine compositions, comprising a di(C-alkyl)-diethylenetriamine of general structure (A), where either R^1 of R^2 is hydrogen and either R^3 or R^4 is hydrogen, and where the remaining two non-hydrogen R groups are independently either: (i) a long chain alkyl group having between 18 to 22 carbon atoms; or (ii) a sh rt chain alkyl group having 8 to 16 carbon atoms; provided that if both alkyl groups on the di(C-alkyl)-diethylenetriamine are long chain (i), r both alkyl groups are short chain (ii), then the compositi n contains a mixture of said structures some of which have l ng chain alkyl groups and some of which have short chain alkyl groups. A method of minimizing trialkanolamine formation in polyalkylenepolyamine compositions is also disclosed.

01 **LOW MELTING POLYALKYLENEPOLYAMINE**

02 **CORROSION INHIBITORS**

03

04 <u>BACKGROUND OF THE INVENTION</u>

05

06 This invention relates to novel hydrocarbon-soluble

07 compositions which are useful in inhibiting corrosion and

08 to a method of preventing corrosion using these

09 compositions. The compositions have desirable low

10 meltpoints.

11

12 Corrosion inhibition has been the subject of considerable

13 interest over many years. The annual cost of replacing

14 corroded metal components is staggeringly high.

15

16 In industrial cleaning operations, where aqueous

17 solutions of acid serve to remove scale and other

18 deposits from metallic surfaces of industrial equipment,

19 inhibitors are used to reduce acid attack on the metals

20 of construction during cleaning operations. In

21 processing operations where some acid is present or may

22 be generated, inhibitors are introduced to reduce the

23 corrosiveness of the acid. In oil well operations,

24 corrosion inhibitors are introduced during various stages

25 and during secondary recovery operations. In all these

26 operations, the corrosion inhibitor is generally in a

27 form which is oil-soluble and dispersible, preferably

28 miscible, in the liquid medium of the particular system.

29

30 Since the industrial equipment being protected by the

31 inhibitor is often of considerable value or is often

32 difficult and expensive to replace, significant

33 importance has been given to the development of new and

34 improved corrosion inhibitors. A wide variety of

35 structures ar currently available in the marketplace.

36

37

2

01 For example, corrosion inhibitors comprised of N-alkyl-
02 amines or polyamines, having alkyl groups in the
03 detergent range, are well known. See, for example, U.S.
04 Patent No. 2,736,658 to Pfohl et al., which discloses
05 aliphatic diamines of the structure:

$$HN(CH_2)_xNH_2$$
$$R$$
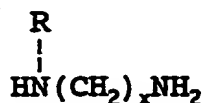
wherein R represents an aliphatic or alicyclic carbon
chain attached to nitrogen of from 8 to 22 carbon atoms
and x is a number from 2 to 10. Preferably, x is 3.
These compounds are described as corrosion inhibitors,
the effectiveness increasing greatly when the diamines
are employed in the form of their fatty or rosin acid
salts.

C-Alkyl diamines are known structures. For example,
Kempter and Moser in J. Prakt. Chem. 34(14), 10411
(1966), CA 66:28324v describe the preparation of even-
numbered 1,2- diamines from chromatographically pure
even-numbered fatty acids. This procedure involves pre-
paring the 2-bromoacid, reacting it with thionyl chloride
and then ammonia to produce the 2-bromoamide, reacting
the amide with 40-80 equivalents of aqueous ammonia to
produce the 2-amino-amide and then reducing this product
with lithium aluminum hydride. Aliphatic 1,2-diamines up
to C_{18} are disclosed.

C-Alkyl polyamines having alkyl groups attached to carbon
are also known structures. For example, U.S. Patent No.
4,293,682 to Kluger et al. discloses triamines are of the
general formula:

$$H_2N-\overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle R^1}{|}}{C}}-CH_2-\overset{\overset{\displaystyle R^3}{|}}{N}-CH_2-\overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}}-NH_2$$
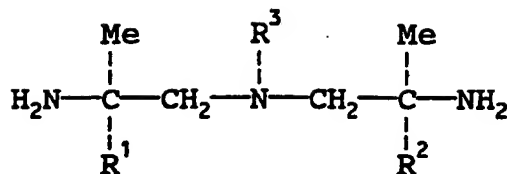
where R^1 and R^2 can be lower alkyl of 1 to 5 carbon atoms and R^3 can be hydrogen. These triamines are useful as epoxy curing agents for polyepoxides

Recently, C-alkyl polyamines have been found to be useful corrosion inhibitors. In particular, U.S. Pat. No. 4,900,458 to Schroeder et al. discloses a polyalkylenepolyamine composition comprising a mixture of components including di(C-alkyl)-diethylenetriamine of the general formula:

$$H_2N-\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{CH}}-CH-N-\overset{\overset{\displaystyle H}{|}}{CH}-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle R_4}{|}}{CH}}-NH_2$$
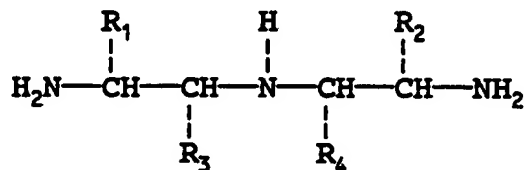
where two of the four R groups are hydrogen, and the other two are alkyl groups independently containing from 10 to 28 carbon atoms. These polyalkylenepolyamine compositions of Schroeder et al., having the alkyl groups attached to carbon rather than nitrogen, exhibit improved corrosion inhibiting characteristics over commercial corrosion inhibitors.

The Schroeder patent (Column 6, lines 22-26) discloses:

"Polyalkylenepolyamines having a mixture of
alkyl groups containing more than one carbon
chain length are especially preferred, as they
have increased solubility, lower melting points
and lower p ur points".

01   In particular, this patent discloses that mixtures of
02   alkyl groups having between 18 and 22 carbon atoms are
03   preferred. Indeed, all 27 examples in U.S. Patent No.
04   4,900,458 produce polyalkylenepolyamines with alkyl
05   groups having 18 to 22 carbon atoms.
06
07   Unfortunately for some applications, the Schroeder et al.
08   compositions are solids, having high meltpoints. They
09   are therefore somewhat difficult to handle, process and
10   formulate. Existing equipment, which is generally used
11   to heat solid materials for handling in a wide variety of
12   operations, often depend on low-pressure steam to provide
13   heat input. For example, oil field service companies
14   have blending facilities which utilize low pressure steam
15   to blend components prior to shipment to the oil field.
16   Schroeder's C-alkyl polyalkylenepolyamine compositions
17   have meltpoints that abut or exceed the ability of this
18   low-pressure steam heating equipment to readily or
19   completely melt these solids. This makes their use
20   difficult or impossible in these situations. Moreover,
21   the long heating times needed to totally melt these
22   solids are undesirable.
23
24   It is an object of this invention to provide
25   polyalkylenepolyamine compositions which melt at
26   temperatures below about 195°F, so that low-pressure
27   steam heating equipment can be used to melt the
28   composition. This will enable customers to readily
29   process, handle and formulate these compositions using
30   their existing equipment.
31
32   I have now discovered that C-alkyl polyalkylenepolyamine
33   compositions comprising di(C-alkyl)-diethylenetriames
34   have surprisingly low meltpoints when the c mposition
35   comprises both long chain alkyl group containing between
36   18 to 22 carbon atoms, and short chain alkyl gr ups
37   containing between 8 to 16 carbon at ms.

5

01   <u>SUMMARY OF THE INVENTION</u>

02

03   The pr sent inv ntion provides a hydrocarbon-soluble,

04   corrosion inhibiting polyalkylenepolyamine composition

05   comprising: a di(C-alkyl)-diethylenetriamine of the

06   general structure

07

08          $H_2N-CHR^1-CHR^2-N-CHR^3-CHR^4-NH_2$

09 |

                                 H

10
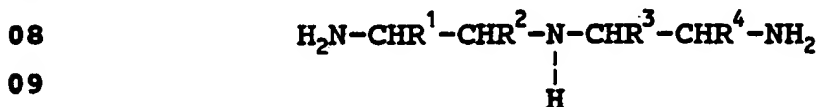
11   where either R^1 or R^2, is hydrogen and either R^3 or R^4 is

12   hydrogen, and where the remaining two non-hydrogen R

13   groups are independently either (i) a long chain alkyl

14   group having between 18 to 22 carbon atoms, or (ii) a

15   short chain alkyl group having between 8 to 16 carbon

16   atoms, provided that if both alkyl groups on the di(C-

17   alkyl)-diethylenetriamine are long chain, (i), or both

18   alkyl groups are short chain, (ii), then the composition

19   contains a mixture of di(C-alkyl)diethylene-triamines,

20   some of which have long chain alkyl groups and some of

21   which have short chain alkyl groups. Preferred

22   compositions of this invention have meltpoints below

23   about 195°F.

24

25   The present invention further provides a method of

26   inhibiting corrosion of a corrodible metal material which

27   comprises contacting the metal material with an effective

28   amount of the corrosion inhibitor composition of the

29   invention.

30

31   The present invention is also concerned with a method of

32   inhibiting corrosion of a corrodible metal material in or

33   around a well through which a corrosive fluid is

34   produced, which comprises contacting the metal material

35   with an effective amount of the corrosion inhibitor

36   composition of the invention.

37

6

01   In one embodiment, the present invention is a method of

02   minimizing trialkanolamine formation in

03   polyalkylenepolyamine compositions having the general

04   structure:

05            $H_2N-CHR^1-CHR^2-N-CHR^3-CHR^4-NH_2$

06                            $\overset{|}{H}$

07
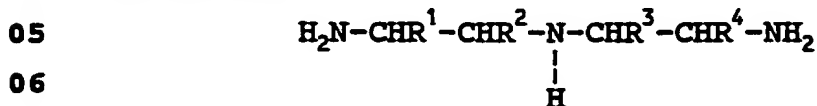
08   where R^1, R^2, R^3 and R^4 are independently hydrogen or an

09   alkyl group having at least 8 carbon atoms comprising,

10   reacting a mixture of alpha-olefin epoxides with ammonia

11   in a reactor wherein 65 to 80% of the reactor volume is

12   liquid, based on calculated liquid volumes at 60°F.

13

14   Among other factors, the present invention is based on my

15   discovery that, for polyalkylenepolyamines corrosion

16   inhibitors comprising di(C-alkyl)-diethyelenetriames

17   which contain a mixture of long chain alkyl groups

18   comprising chain lengths of 18 and 20 carbon atoms and

19   already comprising many different chemical compounds, the

20   meltpoint can be significantly reduced by including short

21   chain alkyl groups of between 8 and 16 carbon atoms on

22   these diethylenetriamines.

23

24   Additionally, the present invention is based on my

25   discovery that, when preparing the polyalkylenepolyamines

26   of this invention from epoxides and ammonia, there is

27   synergy between the reactor fill volume and the ammonia

28   to epoxide ratio. I have discovered that these two

29   factors can be controlled to minimize the formation of

30   undesirable, high- melting trialkanolamines.

31

32   <u>BRIEF DESCRIPTION OF THE DRAWINGS</u>

33

34   Figure 1 is a graph of the meltpoints of various blends

35   of C_{20-24} and C_{14} polyalkylenepolyamines.

36

37

01 Figure 2 is a trace from a DSC instrum nt showing the

02 sec nd DSC endpoint for a polyalkylenepolyamine

03 composition of this invention.

04

05 Figure 3 is an 'H nuclear magnetic resonance spectrum

06 between 2.0 and 4.2 ppm.

07

08   DETAILED DESCRIPTION OF THE INVENTION

09   The Polyalkylenepolyamines

10

11 As used herein the term "long chain alkyl group" (LCAG)

12 denotes an alkyl group having between 18 and 22 carbon

13 atoms. Preferably, the LCAG is a mixture of alkyl

14 groups, and more preferably the mixture contains at least

15 20 mole percent each of alkyl chains having 18 and 20

16 carbon atoms.

17

18 As used herein the term "short chain alkyl group" (SCAG)

19 denotes an alkyl group having between 8 and 16 carbon

20 atoms, or a mixture of alkyl groups having between 8 and

21 16 carbon atoms. Preferably, the SCAG is primarily a

22 single carbon number. Preferred carbon numbers for the

23 SCAG include 10, 12 and 14, more preferably 12 and 14.

24

25 As used herein, the term "C-alkyl" refers to an alkyl

26 group directly bonded to carbon, and the term

27 "di(C-alkyl)" refers to two alkyl groups directly bonded

28 to two different carbon atoms. This usage of "C-alkyl"

29 is similar to the expression "N-alkyl", which is well

30 known in the art and means an alkyl group directly bonded

31 to nitrogen.

32

33 As used herein, the term "unbalanced" or "unsymmetrical"

34 refers to compounds of Structure 2 or 3 (below)

35

36

37

01   comprising both a LCAG and a SCAG on said structure.

02   "Unbalanced" compounds, compositions and structures have

03   at least two alkyl groups, one of which is a LCAG, the

04   other of which is a SCAG.

05

06   In a preferred embodiment, the polyalkylenepolyamine

07   composition of this invention comprises a mixture of

08   structures which includes:

09

10   (a) at least two C-alkylethylenediamines and

11

12   (b) at least two di(C-alkyl)-diethylenetriamines or

13   di(C-alkyl)-piperazines, or a mixture

14   thereof;

15

16   wherein the alkyl groups are unsymmetrical, containing

17   both (i) long chain alkyl groups (LCAG) of between 18 and

18   22 carbon atoms and (ii) short chain alkyl groups (SCAG)

19   of between 8 and 16 carbon atoms.

20

21   Generally, the composition of this invention will contain

22   greater than 10% short chain alkyl groups, and preferably

23   greater than 20%, based on the total number of C-alkyl

24   groups.   The ratio of (i) to (ii) will preferably range

25   from about 0.2:1 to about 3:1, more preferably from 0.3:1

26   to 2:1.

27

28   In a preferred embodiment, the composition contains

29   unbalanced C-alkyl groups (i.e., both long and short

30   chain alkyl groups) on the di(C-alkyl)-diethylenetriamine

31   and the di(C-alkyl)-piperazine. Preferably, the SCAG
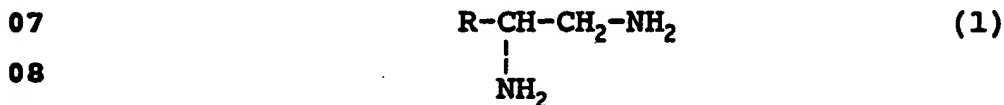
32   contains either 12 or 14 carbon atoms.

33

34

35

36

37

01   Preferred polyalkylenepolyamine compositions of this
02   inv ntion are a mixture of many compounds. This mixture
03   generally includes at least two C-alkyl thylenediamin s
04   of Structure 1 below. The R group in this composition
05   comprises at least one LCAG and at least one SCAG.
06
07                    $R\text{-}CH\text{-}CH_2\text{-}NH_2$ (1)
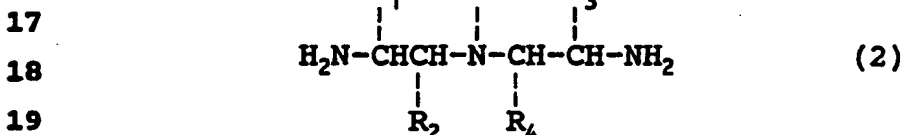08 NH_2
09

10   The composition of this invention includes at least two
11   di(C-alkyl)-diethylenetriamines or di(C-alkyl)-
12   piperazines, or a mixture thereof. At least two
13   di(C-alkyl)-diethylenetriamine of Structure 2 are
14   present.
15

16   R_1 H R_3
17
18        $H_2N\text{-}CHCH\text{-}N\text{-}CH\text{-}CH\text{-}NH_2$ (2)
19   R_2 R_4
20

21   In Structure 2, R_1, R_2, R_3 and R_4 individually may be
22   hydrogen or alkyl, provided that two of the R_1, R_2, R_3 and
23   R_4 groups are hydrogen and two of the R_1, R_2, R_3 and R_4
24   groups are alkyl. Moreover, it is required that the
25   composition contain both LCAG's and SCAG's, either on one
26   molecule or on separate molecules having Structure 2.
27   Preferably, either R_1 or R_2 is hydrogen and either R_3 or R_4
28   is hydrogen.
29

30   The compounds of Structure 2 can also be described as
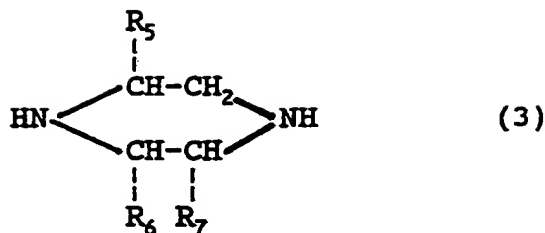31   di(C-alkyl)-2,2'-diamino-diethylamines.
32

33   A cyclized di(C-alkyl) component may also be present, in
34   addition to the di(C-alkyl)-diethylenetriamines.
35   Generally, one or both of the di(C-alkyl)-piperazines of
36   Structure 3 is present:
37

01
02
03
04
05
06

$$HN \diagup \begin{matrix} \overset{R_5}{|} \\ CH-CH_2 \\ CH-CH \\ \underset{R_6 \;\; R_7}{|} \end{matrix} \diagdown NH \qquad (3)$$

07
08 In Structure 3, one of the R_6 and R_7 groups is hydrogen
09 and two of the other of the R_5, R_6 and R_7 groups are
10 alkyl. The composition contains both LCAG's and SCAG's,
11 either on the same molecule or on separate molecules of
12 Structure 3. These di(C-alkyl)-diethylenepiperazines
13 generally include compounds substituted at the 2 and 5
14 position, at the 2 and 6 positions, and at the 3 and 5
15 positions. These compounds may be described as 2,5- 2,6-
16 and 3,5-dialkylpiperazines. It is believed that the
17 above-described dialkyl compounds of Structures 2 and 3
18 are especially advantageous in controlling corrosion.

19
20 It is preferred that the di(C-alkyl)-diethylenetriamine
21 comprise between 5 and 60 mole percent of the total
22 composition, preferably between 5 and 45 mole percent and
23 more preferably between 10 and 40 mole percent. In a
24 preferred embodiment, the alkyl groups on Structure 2 are
25 unbalanced. In this case, the unbalanced di(C-alkyl)-
26 diethylenetriamine comprises between 2.5 and 30 mole
27 percent of the total composition, preferably between 2.5
28 and 23 mole percent and more preferably between 5 and 20
29 mole percent.

30
31 Preferred alkyl groups are derived from the corresponding
32 linear alpha-olefins. Even-numbered alpha-olefins are
33 preferred.

34
35 Particularly preferred polyalkylen polyamin s are
36 mixtures comprising Structure 1 with Structure 2 and/or

37

01 3, where the long chain alkyl group comprises between 25

02 to 75% of the alkyl groups, the remainder being short

03 chain alkyl groups. Thes compositions have desirably

04 lower meltpoints than compositions having only LCAG's.

05

06 As used herein, the term "polyalkylenepolyamine" refers

07 to a mixture of compounds including the alkyldiamine of

08 Structure 1, the higher dialkylpolyamines of Structures 2

09 and 3, and sometimes higher polyalkylenepolyamine

10 oligomers. The alkyl chain can be linear or branched.

11

12 Although Structures 1, 2 and 3 above show primary and

13 secondary amine groups, these amine groups can be

14 substituted with one or more alkyl or amino-alkyl groups.

15 These compounds are also encompassed by the term

16 "polyalkylenepolyamine". As referred to herein, the term

17 "polyamine" and "polyalkylpolyamine" are also used to

18 mean "polyalkylenepolyamine".

19

20 These polyalkylenepolyamines can be present as either the

21 free base or as a salt thereof, such as an organic or

22 inorganic acid salt. Thus, the term

23 "polyalkylenepolyamine" is also meant to include the free

24 base, the ammonium salt form, or mixtures of the two.

25

26   Preparation of Polyalkylenepolyamine

27

28 The corrosion inhibiting composition of this invention

29 can be prepared by a variety of methods.

30

31 One method, which produces unbalanced polyalkylene-

32 polyamines, comprises:

33

34   a) preparing a mixture of functionalized alpha-

35   olefins having between 10 to 24 carbon atoms and

36

37

01   having both long chain alkyl groups (i) and short

02   chain alkyl groups (ii); and

03

04   b)   reacting said functionalized alpha-olefin mixture

05   with ammonia and optionally an amination catalyst

06   to form a polyalkylenepolyamine composition

07   comprising an unbalanced di(C-alkyl)-

08   diethylenetriamine structure.

09

10 The alkyl groups referred to above exclude the 2 carbon

11 atoms of the starting alpha-olefin. For example, a C_{22}

12 alpha-olefin is converted to an epoxide having a long

13 chain alkyl group of 20 carbon atoms.

14

15 Suitable methods of preparing unbalanced polyalkylene-

16 polyamine composition include, but are not limited to the

17 following: reaction of a suitable mixture of

18 1,2-dihaloalkanes with ammonia, in which the halogen may

19 be chlorine, bromine or iodine; reaction of a suitable

20 mixture of 1-epoxyalkanes with ammonia in the presence of

21 a suitable catalyst, such as Raney nickel; reaction of a

22 suitable mixture of 1-amino-2-alkanols or 2-amino-1-

23 alkanols or mixtures thereof with ammonia in the presence

24 of a suitable catalyst, such as Raney nickel; reaction of

25 a suitable mixture of 1,2-alkanediols with ammonia in the

26 presence of a suitable catalyst, such as Raney nickel;

27 reaction of a suitable mixture of C-alkylaziridines with

28 ammonia.

29

30 In the above-described methods, the functionalized alpha-

31 olefins is a 1,2-dihaloalkane, a 1-epoxyalkane, an amino-

32 alcohol, a 1,2-alkanediol, and an aziridine,

33 respectively.

34

35

36

37

01 The mixture of functionalized alpha-olefins can be
02 prepared in a number of ways. One method comprises
03 converting an alpha-olefin mixture containing alpha-
04 olefins having between 10 t 24 carbon atoms and having
05 both long chain alkyl groups (i) and short chain alkyl
06 groups (ii) into a mixture of functionalized alpha-
07 olefins. Alternatively, a mixture of functionalized
08 alpha-olefins can be prepared by blending functionalized
09 alpha-olefins having LCAG's and SCAG's, for example
10 blending epoxides prior to amination. The blending of
11 functionalized alpha-olefins followed by amination is a
12 preferred method of making unbalanced
13 polyalkylenepolyamines. Suitable mixtures of reactants
14 for preparing the unbalanced composition of this
15 invention are those having both LCAG's and SCAG's. For
16 example, a mixture of C_{20}, C_{22} and C_{14} epoxides.
17
18 A critical factor in determining what constitutes a
19 suitable method for preparing the present composition is
20 that the process must provide for the formation of the
21 above-described di(C-alkyl) components, that is,
22 components of Structure 2 and that both LCAG's and SCAG's
23 are present in the polyalkylenepolyamines product.
24
25 In another embodiment, the polyalkylenepolyamine
26 composition of this invention can be prepared by blending
27 polyalkylenepolyamine compositions containing LCAG's with
28 polyalkylenepolyamine compositions containing SCAG's. In
29 this case, at least two polyalkylenepolyamines are
30 prepared separately and then blended. The ratio of long
31 chain to short chain groups can be adjusted, as required.
32 Thus, one method of making the polyalkylenepolyamine
33 composition of the invention comprises the steps of:
34
35
36
37

01   a)   preparing a first polyalkylenepolyamine
02   composition comprising a di(C-alkyl)-
03   diethylenetriamine where both C-alkyl groups
04   are long chain alkyl groups, containing between
05   18 to 22 carbon atoms; and
06

07   b)   preparing a second polyalkylenepolyamine
08   composition comprising a di(C-alkyl)-
09   diethylenetriamine where both C-alkyl groups
10   are short chain alkyl groups, containing
11   between 8 to 16 carbon atoms; and
12

13   c)   blending said first and said second
14   compositions.
15

16 Polyalkylenepolyamine compositions prepared by blending
17 do not result, however, in as great a meltpoint reduction
18 as do compositions containing unbalanced
19 polyalkylenepolyamine.
20

21   <u>Preparation from 1-Epoxyalkanes</u>
22

23 A preferred method of preparing the poly-
24 alkylenepolyamines of the invention is by reaction of a
25 suitable mixture of 1-epoxyalkanes with ammonia in the
26 presence of a suitable amination catalyst, such as Raney
27 nickel. In general, the 1-epoxyalkane mixture will
28 contain from 10 to 24 carbon atoms. Epoxides containing
29 20-24 carbon atoms, preferably a mixture of C_{20}, C_{22} and C_{24}
30 epoxides, will produce polyalkylenepolyamines with
31 LCAG's. Epoxides containing 10-18 carbon atoms will
32 produce polyalkylenepolyamines with SCAG's. The
33 1-epoxyalkane employed for the SCAG is preferably a
34 single carbon number, while the 1-epoxyalkane employed
35 for the LCAG is preferably a mixture of several carbon
36

37

01 numbers. The 1-epoxyalkanes may be branched or linear.

02 Particularly useful 1-epoxyalkanes are derived from

03 epoxidation of alpha-olefins obtained from the ethylene

04 growth reaction.

05

06 The polyalkylenepolyamine composition of the invention

07 can be prepared using procedures similar to those

08 described in U.S. Patent No. 4,900,458, to Schroeder et

09 al., which is incorporated herein by reference in its

10 entirety. Additionally, sample preparations are found in

11 the Examples.

12

13 While not wishing to be bound by theory, it is important

14 to note that polyalkylenepolyamines prepared from a

15 single carbon number 1-epoxyalkane, ammonia and a Raney

16 nickel amination catalyst include a wide variety of

17 compounds. Initial ring opening of the epoxide with

18 ammonia produces two possible amino-alcohols. It is

19 believed that the primary product is the 1-amino-2-ol.

20 Both amino-alcohols yield one diamine when further

21 reacted with ammonia in the presence of the amination

22 catalyst.

23

24 Alternatively, the basic amine of the amino-alcohols can

25 react with a second mole of epoxide to produce three

26 isomeric dihydroxyamine dimers. Amination of these

27 dimers yields the di(C-alkyl)-diethyelenetriamines.

28 Under the reaction conditions, these dimers can also

29 undergo ring closure to piperazines. Similarly trimers

30 and tetramers can also be produced, depending on the

31 ratio of ammonia to epoxide. Moreover, amination of the

32 various amino-alcohols and polyhydroxyamines is generally

33 not complete. Thus, a single carbon number 1-epoxyalkane

34 yields a polyalkylenepolyamine composition containing a

35 wide variety of compounds. These includ :

36

37

01   A. one C-alkylethylenediamine;
02   B. three di(C-alkyl)-diethylenetriamines (various
03   positional isomers);
04   C. two di(C-alkyl)-piperazines (positional isomers);
05
06   D. two amino-alcohols, which are formed by
07   incomplete amination, the 1-amino-2-ol
08   predominates;
09   E. a variety of tri(C-alkyl)-triethylenetetra-
10   amines;
11   F. a triamine species of Structure 4; and
12
13   OH
                            | (4)
14 |
                      N-(CH₂-CH-R)₃
15
16   G. a variety of di(C-alkyl)-hydroxydiamines and
17   -dihydroxyamines, which are also formed by
18   incomplete amination.
19
20   To summarize, a single carbon number 1-epoxyalkane gives
21   about 15 different compounds in various ratios under
22   typical reaction conditions. This ratio of products can
23   be adjusted by changing reaction temperatures, reaction
24   times and ammonia to epoxide ratio.
25
26   When two different 1-epoxyalkanes (i.e., epoxides having
27   two different carbon numbers, such as a mixture of C_{18} and
28   C_{20} epoxides) are mixed and reacted with ammonia, the
29   number of compounds produced increases more than just
30   twofold. The dimer and trimer products (B, C, E, F and G
31   above) can now have alkyl groups with more than one
32   carbon number, resulting in products with mixed chain
33   length alkyl groups. These additional products, further
34   increase the number of chemical compounds produced.
35
36
37
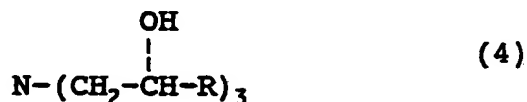
17

01   A mixtur of three epoxides, such as a mixture of C_{20}, C_{22}

02   and C_{24} epoxides, will give polyalkylenepolyamines which

03   ar a mixture of at least 50 different compounds! It is

04   believed that this polyalkylenepolyamine mixture

05   primarily contains C-alkylethylenediamines (3 compounds)

06   and di-(C-alkyl)-diethylenetriamine (18 compounds) and

07   triamines of Structure 4 (8 compounds).

08

09   Surprisingly and unexpectedly, adding a single

10   1-epoxyalkane having a short chain alkyl group to the

11   starting mixture of LCAG 1-epoxyalkanes has a significant

12   effect on the properties of the produced

13   polyalkylenepolyamine. Indeed, the effect of adding a

14   short chain epoxide is dramatic. It results in a drop in

15   meltpoint of 15 to 20°F, over the polyalkylenepolyamine

16   produced from a mixture of long chain alkyl groups, such

17   as those from C_{20}, C_{22} and C_{24} 1-epoxides. Thus, by adding

18   an effective amount of C_{12}, C_{14}, or C_{16} epoxide starting

19   material, an unbalanced di-(C-alkyl)-diethylenetriamine

20   is produced where one of the two alkyl groups is short

21   and the other is long and thereby gives desirable low

22   melting corrosion inhibitors. The differential scanning

23   calorimetry (DSC) second endpoint is used herein as an

24   equivalent measure of the meltpoint.

25

26   Data from polyalkylenepolyamines with different alkyl

27   chain lengths are shown in the following Table. The

28   experimental procedures are detailed herein below.

29

30

31

32

33

34

35

36

37

TABLE 1 - POLYALKYLENEPOLYAMINE DSC ENDPOINTS

Ex. No.	Alkyl chain length[1,2] No. of Carbons	DSC 2nd Endpoint, °F
3	12	201
4	14	203
5	18,20 22 (52:40:7) mix	205
6	0.5 x_i Ex. 1; 0.5 x_i Ex. 5	181

[1] From epoxide starting materials having two additional carbon atoms.

[2] x_i = mole fraction

As can be seen, polyalkylenepolyamines produced with SCAG, i.e., R = C_{12} (from a C_{14} epoxide starting material) or C_{14} have about the same high melting point (203°F) as polyalkylenepolyamines produced with LCAG, i.e., R = C_{18-22} (from a mixture of C_{20}, C_{22}, and C_{24} epoxide starting materials). Surprisingly and quite unexpectedly, polyalkylenepolyamines produced from a blend of these short chain and long chain epoxide starting materials have a meltpoint that is 5-25°F lower, i.e., less than about 200°F. More preferably the compositions of this invention have meltpoints below 195°F, and most preferably below 190°F.

The presently described reaction of 1-epoxyalkanes and ammonia is normally carried out in a single reactor at a temperature in the range of about 100 to 250°C, preferably in the range of about 150 to 230°C and most preferably in the range of about 160 to 190°C. The thermal reaction, epoxide ring opening occurs at about 120°C. The catalytic reaction, amination, is preferably conducted at about 185°C. The reaction pressure is generally in the range of about 500 to 3,000 psi, and preferably between about 1,500 to 2,500 psi.

01 The reactor is normally charg d at room temp rature with

02 hydrogen gas to a pressure of about 10 to 400 psi, and

03 preferably to a pressure of about 20 to 50 psi, although

04 hydrogen may not be necessary. The catalyst employed in

05 the reaction may be either supported or unsupported, and

06 is generally present in an amount equal to about 0.1% to

07 30% of the weight of 1-epoxyalkanes, and preferably 1% to

08 10% of the weight of 1-epoxyalkanes. A small amount of

09 water is generally added. The reaction will normally

10 proceed over a period of about 1 hour to 20 hours. The

11 resulting polyalkylenepolyamine is isolated simply by

12 flashing the volatile hydrogen, ammonia and water and

13 filtering off the catalyst while hot.

14

15 It is also envisioned that the reaction may be carried

16 out in a continuous fashion with similar ratios of

17 ammonia, 1-epoxyalkane and hydrogen passing in a plugflow

18 reactor over a bed of solid catalyst. This continuous

19 process may also allow for separate reaction zones for

20 (1) noncatalytic conversion of the 1-epoxyalkane to

21 alkanolamines mixture, for example in a preheater segment

22 of the continuous reaction unit, and (2) catalytic amina-

23 tion of the alkanolamines mixture to polyalkylenepoly-

24 amines.

25

26 Amination catalysts for converting alcohols to amines are

27 known in the art and include nickel-containing and

28 cobalt-containing catalysts. Preferred catalysts includ

29 Raney nickel, nickel chromite, supported cobalt catalysts

30 such as Harshaw-Filtrol Co-0138E, supported nickel-

31 rhenium catalysts such as that described in U.S. Patent

32 No. 4,111,840 and supported nickel catalysts such as

33 Harshaw-Filtrol Ni5136P. More preferred catalysts are

34 supported cobalt and supported nickel-rhenium catalysts.

35 Raney nickel is most preferred.

36

37

01   Amine-coated Raney nickel catalyst can be used, for
02   example, tallow amine-coated Raney nickel. This catalyst
03   can be recycled; the recycled catalyst gives
04   substantially identical product.

06   Minimizing Trialkanolamine Formation

08   It is believed that one important species contributing to
09   high melt point of these polyalkylenepolyamines are
10   trialkanolamines (TAA) of Structure 4. TAA has a very
11   high melting point and a very low solubility in the
12   solvents used to formulate polyalkenepolyamines into
13   active corrosion inhibitors.

15   Surprisingly, the production of these undesirable
16   trialkanolamines can be minimized by

18   1) using a high ammonia to epoxide ratio and
19   2) controlling the reactor fill factor.

21   I have discovered conditions that reduce the amount of
22   TAA formed in the reaction. Additionally, I have also
23   discovered an interaction between two process variables
24   that can be exploited to reduce the amount of TAA formed.

27   An important process variable that controls formation of
28   TAA is the ammonia to epoxide ratio. Increasing the
29   ammonia to epoxide ratio decreases the amount of TAA
30   formed. Preferred ammonia to epoxide ratios are greater
31   than 4 to 1, preferably greater than 6 to 1, and most
32   preferably greater than 9 to 1.

34   Another important variable that influences TAA formation
35   is referred to herein as "reactor fill factor". The

01 reactor fill factor is computed using the densities of

02 each liquid or solid reactant at 60°F. Preferred reactor

03 charges vary from 65 to 80% of the total volume of a

04 batch reactor. The pr f rred and maximum reactor fill

05 factors depend on the reactant molar ratio, the rated

06 pressure of the reactant vessel and process economics.

07

08 It is preferred that the reaction of the mixture of

09 1-epoxyalkanes with ammonia takes place in a reactor

10 where 65 to 80% of the reactor volume is liquid, based on

11 calculated liquid volumes at 60°F; preferably about 75%

12 of the reactor volume is liquid. If the reactor fill

13 factor is too high, pressure limits are encountered.

14

15 I have also discovered that the useful upper limit to the

16 fill factor is about 80%. At fills greater than this

17 value, the reaction vessel can become hydrostatically

18 loaded during the reaction. This results in an extremely

19 rapid pressure increase from inside the vessel. Unless

20 the vessel can withstand very high pressures, the liquid

21 must be vented through a control or relief system, such

22 as a bursting disc rupture. It is believed that this

23 over-pressurization occurs primarily because of the great

24 expansion factor for ammonia liquid over the temperature

25 range used. However since a considerable amount of

26 ammonia dissolves into the hydrocarbon phase, the exact

27 conditions when the system becomes hydrostatically loaded

28 is difficult to predict.

29

30 More importantly, there is a synergistic effect between

31 the ammonia to epoxide mole ratio and the reactor fill

32 factor. The preferred combination of these variables --

33 high ratio and high fill -- results in a TAA content

34 lower than the sum of the individual effects. For

35 example, raising the ammonia to poxide ratio (from 6:1

36

37

01 to 15.6:1) by itself decreases the TAA content from 9.6

02 to 8.0 mole percent. Raising the fill factor from 50% to

03 80% by itself decreases the TAA to 6.2 mole percent. If

04 the effects were additive, one would expect a TAA content

05 of

06

07   9.6 - [(9.6-8.0) + (9.6-6.2)] = 4.6%

08

09 when both the ammonia ratio and the fill factor are

10 raised. Actual data shows TAA contents of about 4.0%

11 when both variables are high. This demonstrates a

12 significant synergistic interaction.

13

14   Adjusting the Hydrophobic-Hydrophilic Ratio

15

16 Advantageously, the hydrophobic-hydrophilic ratio and

17 nitrogen content of the polyalkylenepolyamine product can

18 be readily adjusted by the addition of various amounts of

19 ethylenediamine or a higher polyethylenepolyamine, such

20 as diethylenetriamine, during the reaction with ammonia.

21 Compounds that produce ethylenediamine (such as

22 ethylenedichloride or higher polyethylene-polyamines can

23 also be used. The amount of ethylenediamine or higher

24 polyethylenepolyamine which may be used will generally

25 range from about 1 to 50 weight percent, and preferably

26 from about 10 to 20 weight percent.

27

28   Corrosion Inhibition

29

30 The polyalkylenepolyamines of this invention are good

31 corrosion inhibitors. In comparison with commercial

32 corrosion inhibitors, they show much superior

33 performance.

34

35 For use as corrosion inhibitors, the polyamines of the

36 invention can be applied to the metal surfaces to be

37

01 protected in a variety of ways known to the art. For
02 example, a dilute hydrocarbon solution of the polyamine
03 may be contact d with the metal to be protected, using
04 methods such as dipping, spraying, wiping, and the like.
05 For this method of application, solutions of about 0.1 to
06 10%, preferably from about 0.2 to 1%, by weight of
07 polyalkylenepolyamine, or mixture of polyalkylene-
08 polyamine and other active corrosion inhibiting agents,
09 are employed.
10
11 Alternatively, oil-soluble, water-dispersible
12 formulations of the present polyamines, or mixtures of
13 the polyamines and other active corrosion inhibiting
14 agents, can be added to a corrosive aqueous environment.
15 In this method of application, sufficient amounts of
16 polyamine, or mixture of the polyamine and other active
17 corrosion inhibiting agents, are added to give from about
18 1 to 1,000 ppm, preferably from 10 to 500 ppm, of active
19 corrosion inhibitor in the final solution for continuous
20 methods of treatment. For batch treatment methods, the
21 level of corrosion inhibiting agents is generally between
22 500 and 25,000 ppm, preferably between 1,000 and 10,000
23 ppm.
24
25 Corrosion inhibitors are usually formulated with other
26 components for corrosion inhibiting applications.
27 Preferably, the corrosion inhibiting poly-
28 alkylenepolyamine composition of the present invention
29 will be combined with one or more dimer/trimer acids to
30 provide a formulated product. Dimer/trimer acids are
31 organic acids and are well known in the art. They are
32 typically derived from fatty acids. Examples of
33 dimer/trimer acids include Empol 1024, obtained from
34 Emery Chemicals, Union Camp Century D75 and W stvaco DTC
35 405.
36
37

01   In addition to the polyalkylenepolyamine of the invention
02   and the dimer/trimer acid, corrosion inhibiting
03   formulations may also contain one or more surfactants,
04   one or more alcohols and a hydrocarbon solvent. The
05   surfactant employed may be ionic or nonionic in nature.
06   Generally, nonionic surfactants are preferred. Typical
07   nonionic surfactants include ethoxylated nonylphenols
08   such as Igepal CO-630 and Igepal CO-710, and ethoxylated
09   fatty alcohols such as Tergitol 15-S-9. The hydrocarbon
10   solvent may be any of the known solvents, such as
11   kerosene, diesel fuel, paint thinner, toluene,
12   lubricating oil, and similar materials. A preferred
13   hydrocarbon solvent is a heavy aromatic distillate
14   containing C_9+ aromatics, such as Chevron HAD, sold by
15   Chevron Chemical Company, San Ramon, California.
16   Isopropanol is a typical alcohol.
17
18   Generally, the active corrosion inhibiting agents will be
19   combined with a solvent and a surface active agent to
20   produce a concentrated solution of the corrosion inhi-
21   bitor. In this solution, the polyamine, or mixture of
22   the polyamine and other active corrosion inhibiting
23   agents, will be present in amounts ranging from about 10
24   to 60%, preferably about 30 to 50%, by weight. The
25   amount of solvent present is from about 30 to 80%, and
26   the amount of surfactant is about 1 to 20%, by weight.
27   This concentrated formulation can then be diluted to the
28   desired concentration of the final solution.
29
30   A preferred oil-soluble, water-dispersible formulation
31   will contain about 15 to 30% actives. The term actives
32   as used herein include all components except the
33   hydrocarbon solvent. A typical formulation would include
34   1-20%, preferably 5-10% of the present p lyalkylenepoly
35
36
37

01 amine, an approximately equal amount of a dimer/trimer

02 acid, about 1 to 10% of a nonionic surfactant, and about

03 0 to 5% of an alcohol, such as isopropanol; the remainder

04 is a hydrocarbon solvent, such as Chevron HAD.

05

06 Oil-soluble, water-dispersible formulations of the

07 present polyamines are particularly useful in brine/CO_2 or

08 brine/H_2S environments, such as encountered in oil wells,

09 especially oil wells employing secondary oil recovery

10 techniques.

11

12 The following examples are provided to illustrate the

13 invention in accordance with the principles of this

14 invention but are not to be construed as limiting the

15 invention in any way except as indicated by the appended

16 claims.

17

18   <u>EXAMPLES</u>

19

20   Example 1

21   <u>MEASURING DSC SECOND ENDPOINT OR THE MELTPOINT</u>

22

23 The term meltpoint as used herein is the second DSC

24 endpoint. The meltpoint was determined using

25 differential scanning calorimetry (DSC). A Perkin Elmer

26 DSC-2 Model 3500 instrument was used. About 5-10 mg of

27 sample was heated at a rate of 10°C/min. The heat uptake

28 was measured as a function of time. The second DSC

29 endpoint was determined as the maximum temperature at

30 which the heat-up curve returns to the base line.

31

32 Figure 2 shows how this value is determined graphically.

33 As can be s en, there are several heat uptakes. A

34 baselin , which is determined by the heating rate, can be

35 readily drawn. The bas line on Figure 2 was computer

36 determined. The maximum temperature at which the actual

37

01 heat uptake curve meets this baseline is the second DSC

02 endpoint or meltpoint. This point is labeled "A" on

03 Figure 2.

04

05   Example 2

06   CALCULATION OF REACTOR FILL FACTOR

07

08 Fill factor is computed using the charges and densities

09 of the reaction system components and the reactor free

10 internal volume. The densities used are taken at 60°F.

11 For example:

12

13 Density of C_{14}/C_{20-24} epoxide = 0.846 g/mL @ 60°F

14   ammonia = 0.616 g/mL @ 60°F

15   water   = 1.00 g/mL @ 60°F

16   coated nickel = 1.67 g/mL @ 60°F

17

18 The reactor fill factor for a run charging 323.5 gms

19 epoxide, 185.0 gms ammonia, 19.6 gms of water, and 62.0

20 gms catalyst into a 1000 mL reactor is computed as:

21

22 $$\frac{323.5/0.846 + 185./0.616 + 19.6/1.00 + 62/1.67}{1000 \text{ mL reactor volume}} \times 100 =$$

23

24

25   = 74% reactor fill factor

26

27

28   Example 3
            PREPARATION OF C_{14} POLYALKYLENEPOLYAMINE

29

30 A C_{14} 1-epoxytetradecane (290.3 g, 1.37 mole) was obtain d

31 from Viking Chemical Company under the trade name

32 "Vikalox 14". It was added to a stirred, 1 liter

33 stainless steel autoclave along with 17.6 g (0.98 mole)

34 of deionized water and 62.0 gms of amine coated Raney

35 nickel catalyst. The catalyst was AMCAT-5 from Activated

36 Metals and Chemicals, Inc. The vessel was pressurized to

37

01 25 psig with hydrogen gas. Anhydrous ammonia (232.8 gms,

02 13.7 mole) was then added. This corresponds to an

03 ammonia to epoxyalkane mole ratio of 10:1. This mixture

04 was heated at 185°C for 3.5 hours. Upon completion of

05 the reaction, the excess ammonia and water were vented

06 and condensed at 130°C. The product was decanted from

07 the catalyst. After cooling, it had a meltpoint of

08 197°F. Repeat runs at similar conditions gave product

09 with meltpoints of 199 and 207°F. The average meltpoint

10 for the three runs was 201°F.

11

12   Example 4

13   PREPARATION OF C_{16} POLYALKYLENEPOLYAMINE

14

15 The procedure of Example 3 was followed, except that

16 Vikalox 16, a C_{16} 1-epoxyalkane was used. The

17 polyalkylenepolyamine product had a meltpoint of 210°F.

18 Additional runs at similar conditions gave products with

19 meltpoints of 201 and 199°F. The average meltpoint for

20 the three runs was 203°F.

21   Example 5

22   PREPARATION OF C_{20}-C_{24} POLYALKYLENEPOLYAMINE

23

24 A C_{20}-C_{24} 1-epoxy alkane (352 g, 1.12 mole) was obtained

25 from Viking Chemical Company under the trade name

26 "Vikalox 20-24". The starting olefin, prior to

27 epoxidation, was analyzed by gas chromatography and shown

28 to contain 1.2 mole % C_{18} olefins, 51.6 mole % C_{20} olefin,

29 40.2 mole % C_{22} olefin and 7.0 mole % C_{24} olefin. This

30 mixture was commercially epoxidized. The resulting

31 epoxides were added to a stirred, 1 liter stainless steel

32 autoclave along with 20.2 g (1.12 mole) of deionized

33 water and 60.2 gms of tallow amine coated Raney nickel

34 catalyst (purchased from Activated Metals and Chemicals,

35 Inc.). About 50 weight % of this catalyst is amine. The

36 vessel was pressurized to 20 psig with hydrogen gas.

37

01 Anhydrous ammonia (192.9 gms, 11.3 mole) was then added.

02 This corresponds to an ammonia to epoxyalkane mole ratio

03 of 10:1. This mixture was heated at a rate of about

04 3°/min. until it reached 185°C. This temperature was

05 then maintained for 3.5 hours. Upon completion of the

06 reaction, excess ammonia and water were vented and

07 condensed at 130°C. This product was decanted from the

08 catalyst while hot. After cooling, the product had a

09 meltpoint of 206°F. Several repetitions of this batch

10 preparation under similar reaction conditions produced

11 product with meltpoints of 210, 207, 208, 200, 206, 203,

12 200 and 205°F. The average meltpoint for these nine runs

13 was 205°F. The preparation was repeated on a large scale

14 under similar mole ratio and reaction conditions. The

15 product had a 207°F DSC endpoint.

16

17 Table 1 shows the second DSC endpoints of the products of

18 Examples 3, 4 and 5. As can be seen,

19 polyalkylenepolyamines with long chain alkyl groups (C_{18-}

20 $_{22}$) and polyalkylenepolyamines with short chain alkyl

21 groups (C_{12} and C_{14}) have about the same meltpoints.

22

23   Example 6

24   PREPARATION OF C_{14}/C_{20-24} MIXED POLYALKYLENEPOLYAMINES

25

26 A C_{20-24} 1-epoxyalkane (1188.7 gms) and 812.3 gms of C_{14}

27 epoxyalkane were melted and then mixed together. This

28 corresponded to a 1:1 molar ratio of the epoxyalkane

29 components. A portion (323.5 gms, 1.24 mole) of the

30 above prepared mixture of 1-epoxyalkanes were added to a

31 1 liter stainless steel autoclave with 19.6 gms (1.09

32 mole) of water and 62.0 gms of amine coated Raney nickel

33 catalyst. The reactor was sealed and pressurized to 25

34 psig with hydrogen. Anhydrous ammonia (185 gms, 10.9

35 mole) was then add d. The mixture was stirred vigorously

36 and heated to 185°C and held at that temperature for 3.5

37

01 hours. At the end of the reaction period, the mixture

02 was cooled and the excess ammonia, hydrogen and water

03 v nted and condensed. The agitation was stopped and

04 excess catalyst allowed to settle. The product was

05 decanted from the dense catalyst layer while hot. After

06 cooling the product had a meltpoint of 178°F. This

07 product is an effective corrosion inhibitor. Additional

08 runs obtained under similar conditions had meltpoints of

09 181, 181 and 187°F, for an average of 182°F for the four

10 runs.

11

12 As can be seen by looking at Table 1, mixing long chain

13 and short chain epoxides produces polyalkylenepolyamines

14 with significantly lower meltpoints, here about 20° lower

15 than either polyalkylenepolyamine alone (i.e., compared

16 to Examples 3 and 5).

17

18   Example 7

19   PREPARATION OF BLENDED C_{14} AND C_{20-24} POLYALKYLENEPOLYAMINE

20

21 A C_{14} polyalkylenepolyamine (13.9 gms, 0.0317 mole),

22 prepared as in Example 3 above and having a meltpoint of

23 197°F, and 61.1 gms (0.0961 mole) of C_{20-24}

24 polyalkylenepolyamine, prepared as in Example 5 above and

25 having a meltpoint of 207°F, were melted separately and

26 then thoroughly blended. The DSC behavior of the blended

27 polyalkylenepolyamines (PAPA's) was determined and is

28 shown in Table 2.

29

30 Additional blends were made using different ratios of the

31 polyalkylenepolyamines. The results are summarized in

32 Table 2 below and shown in Figure 1. Figure 1 is a graph

33 of meltpoint vs mole fraction for a blend of C_{20-24} and C_{14}

34 polyalkyl nepolyamines. As can be seen, some reduction

35 in meltpoint of the C_{20-24} polyalkylenepolyamine can be

36 achieved by blending a C_{14} polyalkylenepolyamine.   All

37 these blends are effective corrosion inhibitors.

TABLE 2 - POLYALKYLENEPOLYAMINE (PAPA) BLENDS

Blend	C_{14} PAPA grams	C_{20-24} PAPA grams	C_{14} PAPA mole %	C_{20-24} PAPA mole %	DSC endpoint °F
7A	13.9	61.1	25	75	206
7B	30.5	44.5	50	50	198
7C	46.1	28.9	70	30	191

Example 8

PREPARATION OF C_{14}/C_{20-24} MIXED POLYALKYANOLAMINES

HIGH AMMONIA, LOW REACTOR FILL FACTOR

A mixture of C_{20-24} 1-epoxyalkane and C_{14} epoxyalkane, 0.5 mole fraction each, were melted and mixed together and corresponded to a 1:1 molar ratio of the epoxyalkane components having a molecular weight of 261. A portion (173.9, 0.67 mole) of the above prepared mixture of 1-epoxyalkanes were added to a 1 liter stainless steel autoclave equipped with external electric based heaters, internal agitator and cooling coils with 6.7 gms (0.37 mole) of water. The reactor was sealed and pressurized to 25 psig with hydrogen. Anhydrous ammonia (177.7 gms, 10.43 mole) was then added (mole ratio of ammonia to epoxide of 15.7). The reactor fill factor was 50%. The mixture was stirred vigorously and heated to 365°F and held at that temperature for 3.5 hours. At the end of the reaction period, the mixture was cooled and the excess ammonia, hydrogen and water vented and condensed. The product was analyzed for TAA content by proton NMR measuring the absorption for the hydrogen atoms alpha to the nitrogen (i.e. those on the number 1 carton atoms) as in Example 11. The product had 5.8 mole % TAA.

Example 9

PREPARATION OF C_{14}/C_{20-24} MIXED POLYALKYANOLAMINES

HIGH AMMONIA, HIGH FILL

The procedure of Example 8 was followed except that 278 g of epoxide, 284 g of ammonia (mole ratio 15.7) 10.89 of water were used to give a reactor fill factor of 80%. The product contained 4.1% TAA.

Example 10

PREPARATION OF C_{14}/C_{20-24} MIXED POLYALKYANOLAMINES

ADDITIONAL EXPERIMENTS

Additional experiments were performed at various ammonia to epoxide mole ratios and reactor fill factors using the procedure of Example 8 and the amounts of reactants shown in Table 3.

Table 3 shows four pairs of runs, each of which have the same ammonia ratio and fill factor, and differ (within the pair) by the water ratio. The water ratio was determined to have no effect on the TAA content. Thus, the TAA content for each pair can be averaged to show the interaction effect.

TABLE 3

Alkanolamine Runs Using C_{14}/C_{20-24} Blended Epoxides

Design order	Feeds, grams charged			H2, psig	Mole ratio		Fill[1] factor	TAV[2]	TAA[3]
	Epoxide	NH3	Water		NH3	H2O			
1	173.9	177.7	6.72	25	15.7	0.56	0.50	149	5.8
2	424.1	154.7	49.15	25	5.6	1.68	0.80	141	8.5
3	265.1	96.7	30.7	25	5.6	1.68	0.50	132	9.7
4	271.0	276.8	31.4	25	15.7	1.68	0.80	160	3.8
5	442.2	161.3	17.1	25	5.6	0.56	0.80	138	7.6
6	278.0	284.0	10.75	25	15.7	0.56	0.80	154	4.1
7	276.0	100.8	10.8	25	5.6	0.57	0.50	127	9.4
8	169.4	173.0	19.6	25	15.7	1.68	0.50	141	6.7

[1] Fill Factor %/100%

[2] TAV = Total Amine Value

[3] TAA = Trialkanolamine

The data from Table 3 is simplified in Table 4 below.

TABLE 4

Pair	Ratio[1]	Fill[2]	Avg. TAA, %
4 & 6	High	High	4.0
2 & 5	Low	High	6.2
1 & 8	High	Low	8.0
3 & 7	Low	Low	9.6

[1] Ammonia to epoxide ratio
[2] Reactor fill factor

As can be seen, high ammonia to epoxide ratios and high reactor fill factors give reduced amounts of TAA. Since TAA has a high meltpoint, low solubility, and does not further aminate to give polyalkylenepolyamines, it is desirable to minimize its production.

The mixture of products produced in Examples 8, 9 and 10 can be further aminated with ammonia and Raney nickel to give polyalkylenepolyamines of this invention. The polyalkylenepolyamines produced at high mole ratios and high fill factors will have lower meltpoints.

Example 11

TRIALKANOLAMINE CONTENT BY NMR

Proton NMR spectra were used to quantitate alkanolamine conversion, selectivity to polyalkylenepolyamines and trialkanolamine (TAA) formation.

A General Electric QE-300 Plus NMR spectrometer with a 5mm dual (^{13}C and ^{1}H) probe was used. The samples were dissolved and heated to 50°C in chloroform to keep the TAA in solution.

The most prominent features in the spectrum are:

01   1)   The large methylene envelope between 1.0-1.5

02   ppm,

03   2)   The methyl triplets at about 0.75 ppm, and

04   3)   The functional groups of interest ($\underline{H}$-C-NRR' and

05               $\underline{H}$-C-OH) located between 2.0-4.0 ppm.

06

07   The major spectral features are due to methyl and

08   methylene absorbances since those groups comprise the

09   majority of the molecule.

10

11   Figure 3 is an expansion of an NMR spectrum showing the

12   amine/alcohol absorbance region of interest (2.0-4.0

13   ppm). There are three sets of doublets of doublets (4

14   peaks in each set) between 2.7 and 3.0 ppm which can be

15   used to calculate both the conversion and selectivity.

16   Each of these doublets of doublets corresponds to a

17   single proton in the molecule. The heights of these

18   peaks are used to calculate both the residual reactive

19   alkanolamine and the piperazine content.

20

21   The first set is found between 2.7-2.8 ppm. It is

22   associated with the desired amine product. The second

23   set (2.8-2.9 ppm) is associated with reactive primary and

24   secondary alkanolamines. The third set (2.9-3.0 ppm) is

25   associated with piperazine by-products.

26

27   Two clusters of peaks between 3.4-3.8 ppm correspond to

28   the protons attached to hydroxyl carbons ($\underline{H}$-C-OH). The

29   broad peak between 3.4-3.55 is assigned to the primary

30   and secondary alkanolamines (AA). The broad peak between

31   3.55-3.8 ppm is due to the trialkanolamine (TAA) $\underline{H}$-C-OH

32   protons.

33

34   The mole percent TAA is calculated by the following

35   formula:

36

37        $\text{Mole \% } = 100 \text{ x } \dfrac{\text{integrated area of TAA peaks}}{\text{integrated area between 2.0-4.0 ppm}}$

01 TAA content is calculated from the spectrum integration
02 over the expanded range of 2.0-4.0 ppm.
03
04 Other embodiments of the invention will be apparent to
05 those skilled in the art from a consideration of this
06 specification or practice of the invention described
07 therein. It is intended that the specification and
08 examples be considered as exemplary only, with the true
09 scope and spirit of the invention being indicated by the
10 following claims.
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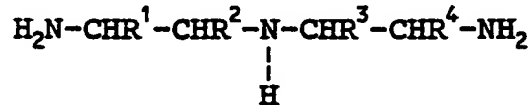35
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01   WHAT IS CLAIMED IS:

02

03   1. A corrosion-inhibiting polyalkylenepolyamine

04   composition comprising: a di(C-alkyl)-

05   diethylenetriamine of the general structure

06

07              $H_2N-CHR^1-CHR^2-N-CHR^3-CHR^4-NH_2$

08 |
                                   H

09

10   where either R^1 or R^2 is hydrogen and either R^3 or R^4

11   is hydrogen, and where the remaining two non-

12   hydrogen R groups are independently either:

13

14   (i)   a long chain alkyl group having between 18 to

15   22 carbon atoms; or

16   (ii)   a short chain alkyl group having between 8 to

17   16 carbon atoms;

18

19   provided that, if both alkyl groups on the di(C-

20   alkyl)-diethylenetriamine are long chain, (i), or

21   both alkyl groups are short chain, (ii), then the

22   composition contains a mixture of di(C-

23   alkyl)diethylenetriamines, some of which have long

24   chain alkyl groups and some of which have short

25   chain alkyl groups.

26

27   2. The polyalkylenepolyamine composition according to

28   claim 1 wherein said di(C-alkyl)-diethylenetriamine

29   is unbalanced, having one long chain alkyl group

30   from (i) and one short chain alkyl group from (ii).

31

32   3. The polyalkylenepolyamine composition according to

33   claim 1 where the short chain alkyl group has 8 to

34   14 carbon atoms.

35

36

37

01 4. The polyalkylenepolyamine composition according to
02 claim 3 where the short chain alkyl group has 10 to
03 12 carbon atoms.
04
05 5. The polyalkylenepolyamine composition according to
06 claim 1 where said di(C-alkyl)-diethylenetriamine
07 comprising between 5 and 60 mole percent of the
08 total composition.
09
10 6. The polyalkylenepolyamine composition according to
11 claim 5 where the mole percent of said di(C-alkyl)-
12 diethylenetriamine comprises between 5 and 45 mole
13 percent of the total composition.
14
15 7. The polyalkylenepolyamine composition according to
16 claim 6 where the mole percent of said di(C-alkyl)-
17 diethylenetriamine comprises between 10 and 40 mole
18 percent of the total composition.
19
20 8. The polyalkylenepolyamine composition according to
21 claim 2 where the mole percent of said unbalanced
22 di(C-alkyl)-diethylenetriamine comprises between 2.5
23 and 30 mole percent of the total composition.
24
25 9. The polyalkylenepolyamine composition according to
26 claim 8 where the mole percent of said unbalanced
27 di(C-alkyl)-diethylenetriamine comprises between 5
28 and 20 mole percent of the total composition.
29
30 10. The polyalkylenepolyamine composition according to
31 claim 2 having a meltpoint below 195°F.
32
33 11. A polyalkylenepolyamin composition comprising a
34 mixture of structur s which includes:
35
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37

01   (a)   at least two C-alkylethylenediamines and

02

03   (b)   at least two di(C-alkyl)-diethylenetriames or

04   di(C-alkyl)-piperazines, or a mixture thereof;

05   wherein the alkyl groups on (b) are unbalanced

06   containing both (i) long chain alkyl groups of

07   between 18 and 22 carbon atoms and (ii) short

08   chain alkyl groups of between 8 and 16 carbon

09   atoms.

10

11   12. The polyalkylenepolyamine composition according to

12   claim 11 where the short chain alkyl group has 12 to

13   14 carbon atoms.

14

15   13. The polyalkylenepolyamine composition according to

16   claim 11 where the short chain alkyl groups comprise

17   at least 10 percent of the total number of C-alkyl

18   groups.

19   14. The polyalkylenepolyamine composition according to

20   claim 11 where the ratio of (i) to (ii) is in the

21   range of 0.2:1 to 3:1.

22

23   15. A method of making the polyalkylenepolyamine

24   composition of claim 2 which comprises:

25

26   a)   preparing a mixture of functionalized alpha-

27   olefins having between 10 to 24 carbon atoms and

28   having both long chain alkyl groups (i) and

29   short chain alkyl groups (ii); and

30

31   b)   reacting said functionalized alpha-olefin

32   mixture with ammonia and optionally an amination

33   catalyst to form a polyalkylenep lyamine

34   composition comprising an unbalanced di(C-

35   alkyl)-diethylenetriamine structure.

36

37

01   16.   The method of claim 15 wherein said functionalized
02   alpha-olefin mixture is a mixtur of alpha-olefin
03   epoxides.
04
05   17.   The method of claim 16 wherein the long chain alkyl
06   group of said epoxide is a mixture having between
07   18-22 carbon atoms.
08
09   18.   The method of claim 17 wherein the short chain alkyl
10   group of said epoxide has between 10 to 16 carbon
11   atoms.
12
13   19.   The method of claim 18 wherein the short chain alkyl
14   group of said epoxide has between 12 to 14 carbon
15   atoms.
16
17   20.   A method of inhibiting corrosion of a corrodible
18   metal material comprising contacting a metal
19   material with an effective amount of the
20   polyalkylenepolyamine composition of claim 1.
21
22   21.   The method of claim 20 wherein said
23   polyalkylenepolyamine composition comprises a di(C-
24   alkyl)-diethylenetriamine which is unbalanced,
25   having one long chain alkyl group and one short
26   chain alkyl group.
27
28   22.   A method of inhibiting corrosion in an oil well of a
29   corrodible metal material comprising contacting a
30   metal material with an effective amount of the
31   polyalkylenepolyamine composition of claim 1.
32
33   23.   The method of claim 22 wherein said
34   polyalkylenepolyamin composition comprises a di(C-
35   alkyl)-diethylenetriamine which is unbalanced,
36   having one long chain alkyl group and one short
37   chain alkyl group.

01 24. A method of minimizing trialkanolamine formation in
02   polyalkylenepolyamine compositions comprising,
03   reacting an alpha-olefin epoxide or a mixture of
04   alpha-olefin epoxides, having at least 10 carbon
05   atoms, with ammonia in a reactor wherein 65 to 80%
06   of the reactor volume is liquid, based on calculated
07   liquid volumes at 60°F.
08
09 25. The method of claim 24 wherein about 75% of the
10   reactor volume is liquid.
11
12 26. The method of claim 24 where the ratio of ammonia to
13   epoxide is greater than about 6 to 1.
14
15 27. The method of claim 26 where the ratio of ammonia to
16   epoxide is greater than about 9 to 1.
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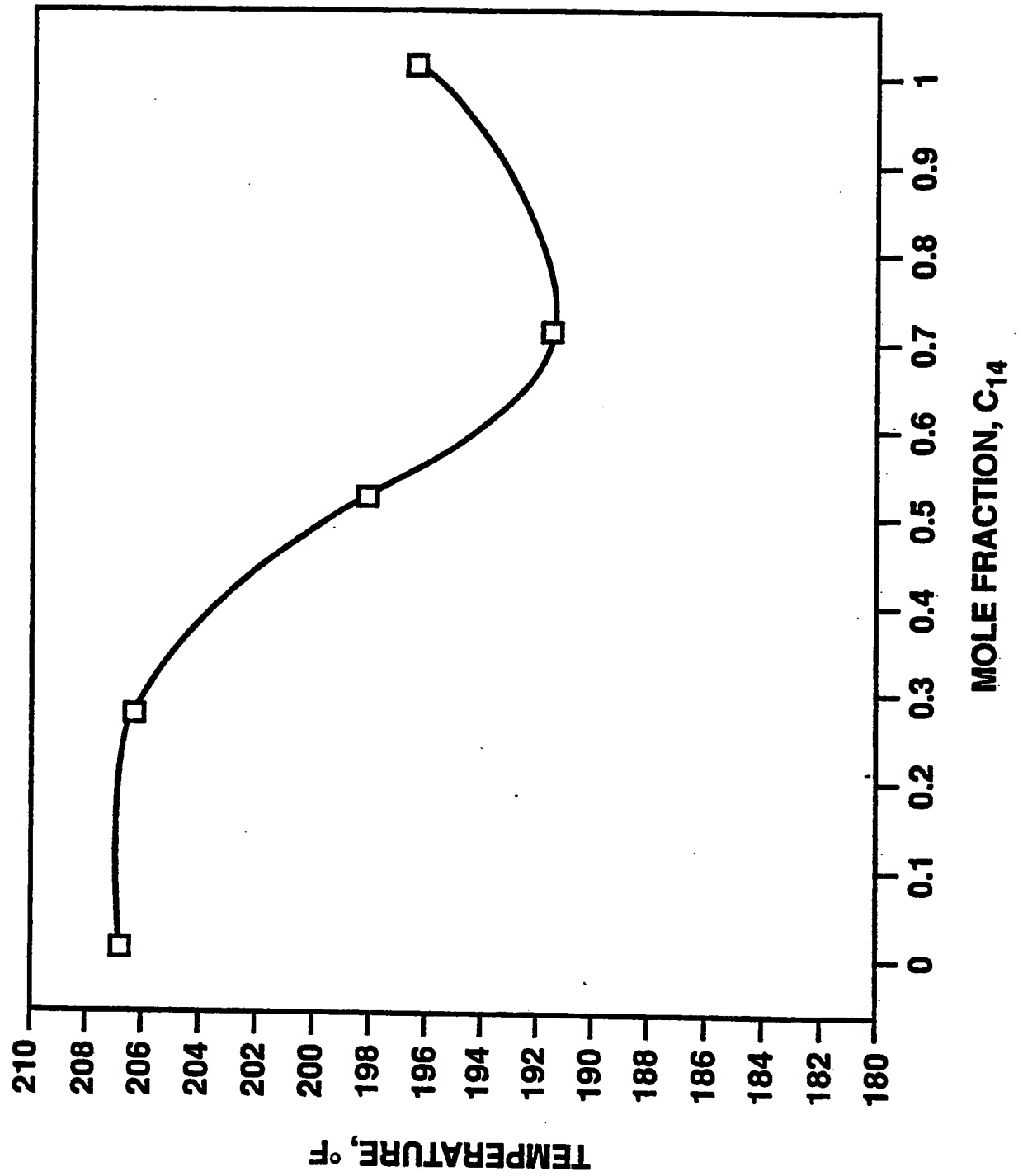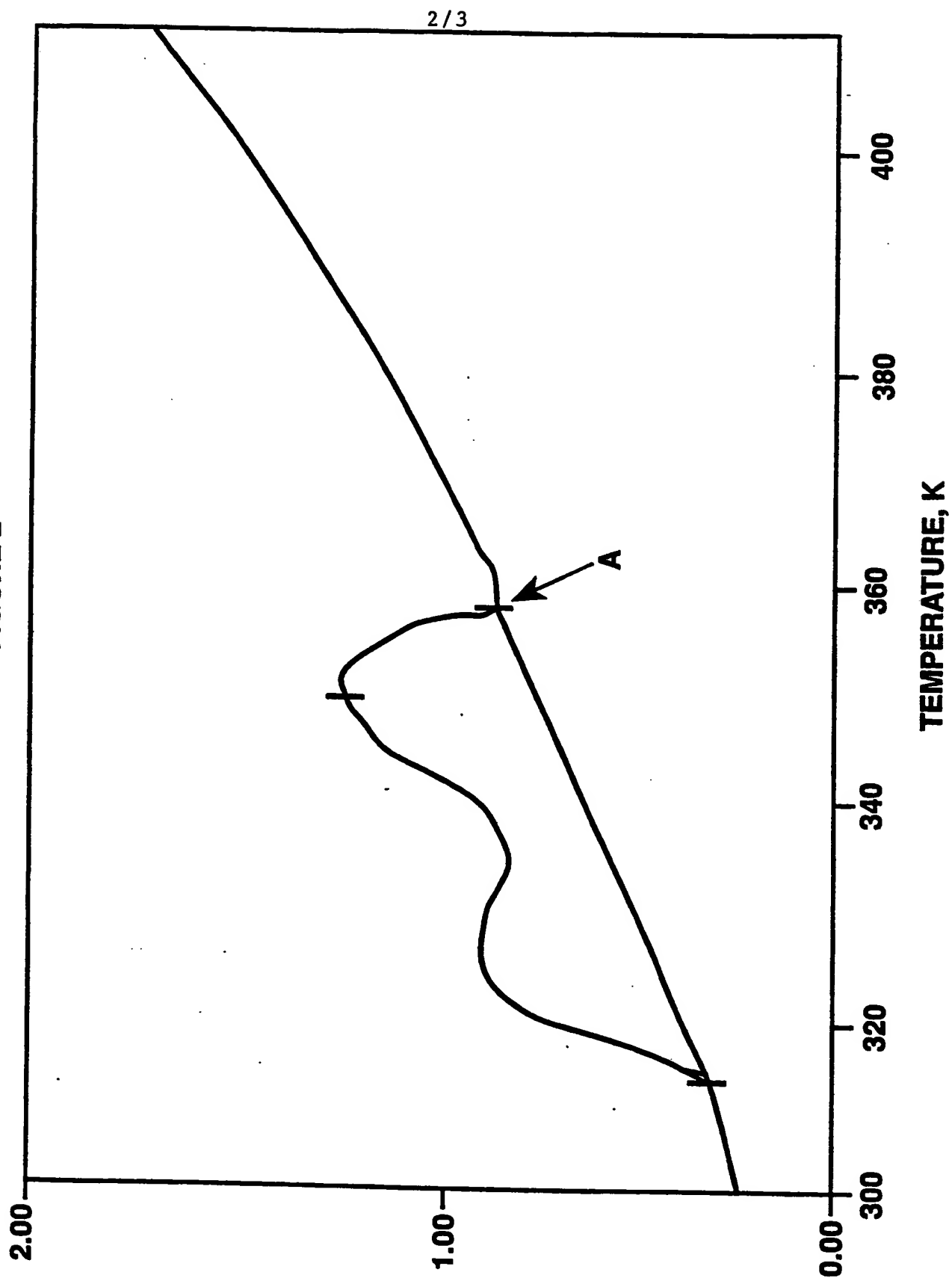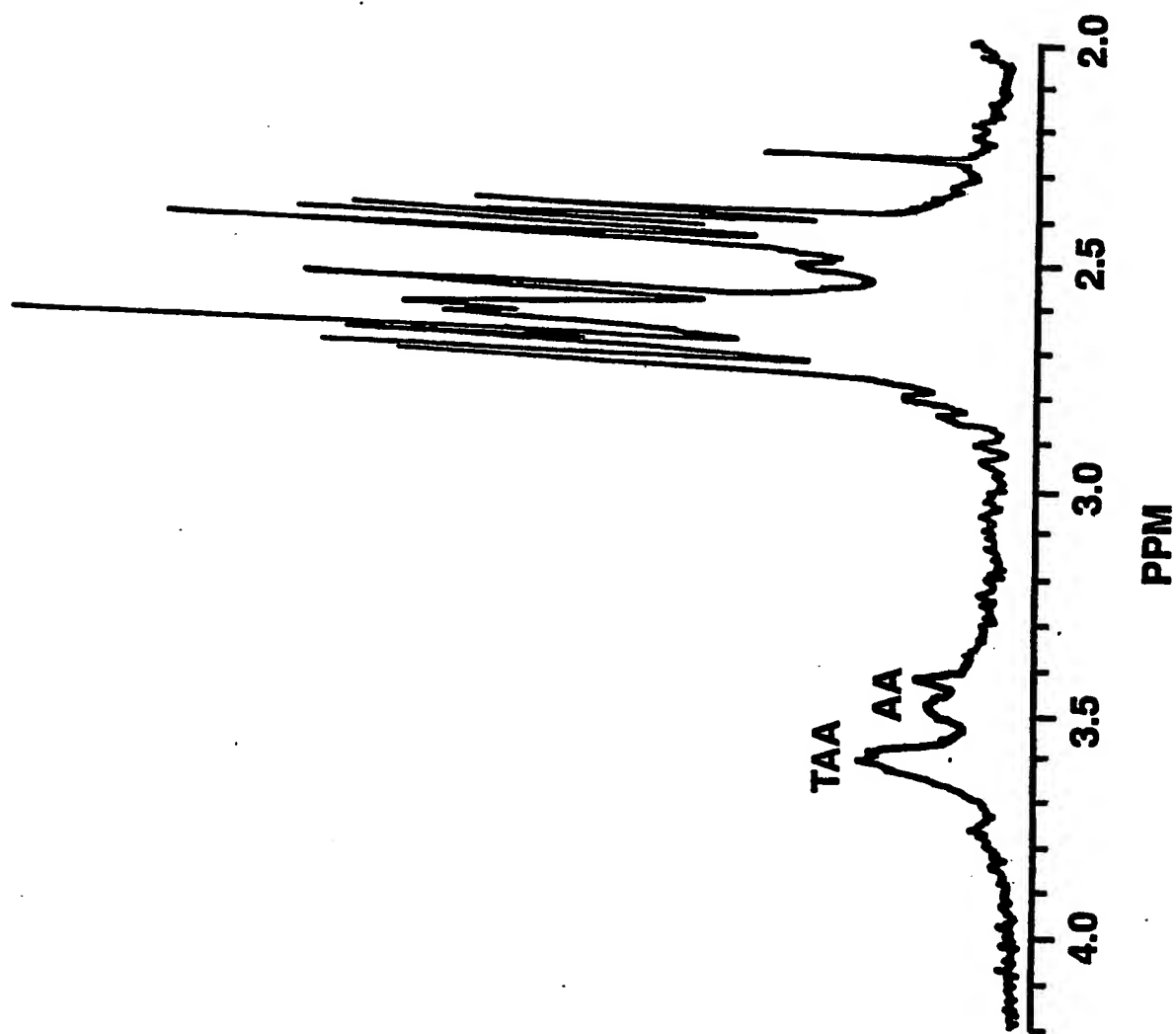21
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FIGURE 1

FIGURE 2

FIGURE 3

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION F SUBJECT MATTER

IPC(5)   :C23F 11/14
US CL   :252/390,8.555;422/16
According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/390,8.555;422/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,900,458 (Schroeder et.) 13 February 1990, see column 41, lines 25-38, col. 5 lines 59-63 and col. 9 lines 65-69.	1-27

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 MAY 1993	0 9 JUN 1993 ₹

Name and mailing address of the ISA/US	Authorized officer M.J. Mears
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	VALERIE FEE